AD

GRANT AF OAR 62 - 34

TN 1

25 July 1963

AD658191

TECHNICAL NOTE NO. 1

HYDRIDO-COMPLEXES OF RHODIUM(I) AND COBALT(I)

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The research reported in this document has been sponsored by the AIR FORCE OFFICE OF SCIENTIFIC RESEARCH, OAR through the European Office, Aerospace Research, United States Air Force. This note is intended only for the internal management uses of the contractor and the Air Force.

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Hydrido-complexes of transition-metals. Part 1. Hydrido-complexes of Rhodium(I) and Cobalt(I).

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Summary

The preparation and properties of complex salts of rhodium(I), of formula $[Rh(C_2H_4\{PPh_2\}_2)_2]X$ (X = Cl, ClO_4, BPh_4), are described. From these a very stable hydrido-complex of rhodium(I), of formula $[RhH(C_2H_4\{PPh_2\}_2)_2]$ is prepared by reduction with lithium aluminium hydride and with sodium borohydride. The product of reaction between $CoBr_2(C_2H_4\{PPh_2\}_2)_2$ and sodium borohydride, previously described as a derivative of cobalt(0), is shown to be a hydrido-complex of cobalt(I), of formula $[CoH(C_2H_4\{PPh_2\}_2)_2]$. This formula is proved by the diamagnetism of the compound, by its infrared spectrum and by its reaction with carbon tetrachloride to give chloroform. The dipole moments, of the order of 3 - 4 D, suggest a non-ortogonal structure for these hydrido-complexes of rhodium and cobalt.

A number of stable hydrido-complexes of transition-metals, of general formula $[MH_xX_yL_z]$, where X is an anionic ligand and L is a tertiary phosphine or arsine, have been prepared in these last years.[1] Among the metals of the cobalt group, many very stable derivatives of iridium [2] and only a few of rhodium [3] are known. The only hydrido-complex of cobalt, stabilised by a tertiary phosphine, is the compound $[CoH(C_2H_4\{PPh_2\}_2)_2]$, which has been recently prepared (together with the corresponding deuteride) in these laboratories [4] by reduction of $CoBr_2(C_2H_4\{PPh_2\}_2)_2$ with lithium aluminium hydride (and deuteride resp.) in tetrahydrofuran.

In this paper we describe the preparation and properties of some complex salts of rhodium(I) of formula $[Rh(DPE)_2]X$ (DPE = 1,2-bis(diphenylphosphino)ethane; X = Cl, ClO_4, BPh_4), the preparation and properties of a new very stable hydrido-complex of rhodium(I), of formula $[RhH(DPE)_2]$, and we prove that the product of the reaction between $CoBr_2(DPE)_2$ and sodium borohydride, previously described[5] as a derivative of cobalt(0), actually is a hydrido-complex of cobalt(I), of formula $[CoH(DPE)_2]$.

The compound $[Rh(DPE)_2]Cl$ is easily prepared from $[Rh(CO)_2Cl]_2$ and the diphosphine in benzene. It is a stable, yellow, crystalline substance, soluble in polar organic solvents, in which it is ionised,

insoluble in hydrocarbons. The corresponding perchlorate and tetraphenyl=borate are readily obtained by exchange in alcoholic solution.

Preparation of Hydrido-complexes. The hydrido-complex of rhodium(I) is obtained by reduction of $[Rh(DPE)_2]Cl$ with lithium aluminium hydride in tetrahydrofuran or with sodium borohydride in ethanol. It is an orange, crystalline compound, rather soluble in benzene, insoluble in alcohols and light petroleum. It shows a considerable thermal stability (m.p. 240°; decomp. 280°), but it is rapidly oxidised by air.

The deuteride is obtained in a similar way with lithium aluminium deuteride in tetrahydrofuran, and it can be recrystallized by adding ethanol to its benzene solution without undergoing any detectable exchange.

The hydrido-complex of cobalt(I), prepared by reduction of $CoBr_2(DPE)_2$ with sodium borohydride either in absolute or in aqueous ethanol, is exactly alike, both before and after recrystallisation from benzene-ethanol and from dimethylformamide, to the compound obtained by reduction with lithium aluminium hydride[4].

Infrared Absorption Spectra. The infrared spectrum of the hydrido-complex of rhodium(I) shows a strong sharp band at 1902 cm^{-1}, due to the metal-hydrogen stretching vibration; the spectrum of the corresponding

deuterido-derivative shows a sharp strong band at 1465 cm^{-1} (ratio of hydride to deuteride stretching frequencies equal to 1.39). Moreover, the spectrum of the hydrido-complex shows a band at 6[illegible]6 cm^{-1} which does not appear in the spectrum of the deuterido-complex, and which we tentatively assign to the bending mode δ(Rh-H).

The infrared spectrum of the hydrido-complex of cobalt(I) shows a band of medium intensity at 1884 cm^{-1}, ascribable, by comparison with the spectrum of the corresponding deuteride(4), to the stretching mode ν(Co-H).

The increase in M-H stretching frequencies, found going from cobalt to rhodium, is in agreement with the increase of M-H bond strength generally observed in passing from the light to the heavy elements.

<u>Reactions</u>. The hydrido-complex of rhodium(I) reacts at room temperature with carbon tetrachloride according to:

$$[RhH(DPE)_2] + CCl_4 = [Rh(DPE)_2]Cl + CHCl_3$$

and with perchloric acid, in aqueous ethanol, giving off hydrogen according to the equation:

$$[RhH(DPE)_2] + HClO_4 = [Rh(DPE)_2]ClO_4 + H_2$$

By treating the hydride with hydrogen chloride in the same conditions, it still reacts giving off hydrogen in a molar ratio hydrogen to complex of 1 to 1, but the product of the reaction contains two atoms of

chlorine per atom of rhodium and behaves as a uni-univalent electrolyte. This compound is diamagnetic and shows in the infrared spectrum a weak band in the region of the metal-hydrogen stretching vibrations, i.e. at 2110 cm^{-1}. The same compound is also obtained by treating $[Rh(DPE)_2]Cl$ with hydrogen chloride in ethanol under nitrogen, and therefore we consider it as a hydrido-complex of trivalent rhodium, formed as follows:

$$[RhH(DPE)_2] + HCl = [Rh(DPE)_2]Cl + H_2$$

$$[Rh(DPE)_2]Cl + HCl = [RhHCl(DPE)_2]Cl$$

Though further studies will be undertaken to prove this formulation, this is supported by the analogous addition of hydrogen chloride to the iridium(I) complexes, according to:

$$[IrCl(CO)(PPh_3)_2] + HCl = [IrHCl_2(CO)(PPh_3)_2] \qquad (6)$$

$$[IrH(CO)(PPh_3)_3] + HCl = [IrH_2(CO)(PPh_3)_3]Cl \qquad (7)$$

and to the platinum(II) complex[8] of formula $[PtHCl(PEt_3)_2]$ to give $[PtH_2Cl_2(PEt_3)_2]$.

The hydrido-complex of cobalt(I) does not give off hydrogen by action of hydrogen chloride or perchloric acid, though reacting giving products still under study. With carbon tetrachloride it gives chloroform and not yet identified cobalt derivatives.

Dipole moments and tructure. The hydrido-complex of rhodium(I) in benzene solution has a moment of 4.35 D, assuming $P_A = 0$, or 4.03 D, assuming $P_A = 0.20\ P_E$. The hydrido-complex of cobalt(I) has a moment of 3.50 D ($P_A = 0$) or 3.08 D ($P_A = 0.20\ P_E$).

The values of the dipole moments (4.2 - 4.9 D) determined by Chatt[1] for the hydrido-complexes of the type trans-$[PtHCl(PR_3)_2]$ and trans-$[MHCl(C_2H_4\{PEt_2\}_2)_2]$ (in which M = Fe, Ru, Os) indicate that the metal-hydrogen bond moment is certainly less than 2 D, and, owing to the increased negative character of the trans-halogen under the influence of the hydride ligand, probably much less than 2 D. Therefore, we can exclude for the hydrido-complexes of rhodium(I) and cobalt(I) a tetra= gonal structure with the four phosphorous atoms on the same plane of the metal. The values of the dipole moments of these hydrido-complexes rather suggest a distorted tetrahedral arrangement of the phosphorous atoms surrounding the central metal atom, with the hydrogen atom situated along a trigonal axis. This type of structure, similar to that proposed for the cobalt tetracarbonyl hydride[9], would account for the asserted isomorphism of Chatt's compound[5], now shown to be a hydrido-derivative, with the tetracoordinated complexes of nickel(0) and palladium(0) with the same diphosphine.

The compounds here described represent the first example of very

stable hydrido-complexes with a non-ortogonal configuration and with the metal in the oxidation state +1.

Nuclear Magnetic Resonance. The spectra of the hydrido-complexes, carried out in deuterated benzene with the Varian 4310 C apparatus, did not show any band assignable to the proton resonance of the hydridic hydrogen, probably for one or more of the following reasons: poor solubility of the compounds in benzene; inadequate sensitivity of the apparatus; splitting of the hydrogen band in a number of very weak bands, owing to the interaction of the proton with the phosphorous nucleii of spin 1/2. The very sharp bands shown by the C_6H_5 and CH_2 groups of the ligand confirm the diamagnetism of these compounds, indipendently determined by Gouy's method.

Experimental

The diphosphine $(CH_2.PPh_2)_2$ was prepared as described by Chatt and Hart[10]. The hydrido-complexes were manipulated in an atmosphere of dry nitrogen, and their m.p.s were determined in evacuated tubes. The infrared spectra were obtained in Nujol with the Perkin-Elmer 237 spectrometer.

Di-{1,2-bis(diphenylphosphino)ethane} rhodium(I) chloride $[Rh(C_2H_4(PPh_2)_2)_2]$ Cl. A solution of the diphosphine (3.1 g., 2 mols) in benzene (20 c.c.) was added to a solution of $[Rh(CO)_2Cl]_2$ (0.7 g., 1 mol) in benzene.

The resulting yellow precipitate was collected, washed with warm benzene and dried. The compound is diamagnetic, soluble in chloroform, methylene chloride, methanol, ethanol and acetone, insoluble in benzene and light petroleum. m.p. 215° (Found: C, 66.70; H, 5.19; Cl, 3.80; $C_{52}H_{48}ClP_4Rh$ requires C, 66.77; H, 5.17; Cl, 3.79%). Molar conductivity 10^{-3} M in nitrobenzene at 28°: λ_m = 24.0 mhos.

Di-{1,2-bis(diphenylphosphino)ethane}rhodium(I) perchlorate

$[Rh(C_2H_4\{PPh_2\}_2)_2]ClO_4$. A solution of the chloride described above, in ethanol, was treated with an ethanolic solution of sodium perchlorate. The resulting golden-yellow precipitate was collected, washed with ethanol and dried. m.p. 282° (Found: C, 61.75; H, 4.74; Cl, 3.63; $C_{52}H_{48}ClO_4P_4Rh$ requires C, 62.49; H, 4.84; Cl, 3.55%). Molar conductivity 10^{-3} M in nitobenzene at 25°: λ_m = 21.6 mhos.

Di-{1,2-bis(diphenylphosphino)ethane}rhodium(I) tetraphenylborate

$[Rh(C_2H_4\{PPh_2\}_2)_2]BPh_4$, was similarly prepared from the chloride and sodium tetraphenylborate. Light yellow powder, m.p. 246°. (Found: C, 75.3; H, 5.76; $C_{76}H_{68}BP_4Rh$ requires C, 74.88; H, 5.62%). Molar conductivity 10^{-3} M in nitrobenzene at 25°: λ_m = 15.7 mhos.

Hydridodi-{1,2-bis(diphenylphosphino)ethane}rhodium(I) $[RhH(C_2H_4\{PPh_2\}_2)_2]$

a) A solution of $[Rh(DPE)_2]Cl$ (2.0 g., 1 mol) in ethanol (40 c.c.) was treated with a solution of sodium borohydride (0.24 g., 3 mols) in

ethanol (30 c.c.) under nitrogen. The resulting orange crystalline precipitate was filtered, dried and crystallised from benzene by adding ethanol. Diamagnetic orange plates, m.p. 242°, decomp. 280°, soluble in benzene, insoluble in ethanol, methanol, light petroleum. (Found: C, 69.25; H, 5.62; P, 14.1; $C_{52}H_{49}P_4Rh$ requires C, 69.33; H, 5.48; P, 13.75%).

b) A solution of $[Rh(DPE)_2]Cl$ (1.0 g., 1 mol) in tetrahydrofuran (30 c.c.) was treated with an excess of lithium aluminium hydride in tetrahydrofuran under nitrogen. The original yellow solution rapidly became orange and ethanol was then slowly added until effervescence ceased. The solvent was removed at 6 mm and from the benzene-soluble portion of the residue the orange complex was precipitated with ethanol. The compound was identified by its infared spectrum.

<u>Deuteridodi-{1,2-bis(diphenylphosphino)ethane}rhodium(I)</u>, was similarly prepared in tetrahydrofuran from $[Rh(DPE)_2]Cl$ and lithium aluminium deuteride.

<u>Hydridodi-{1,2-bis(diphenylphosphino)ethane}cobalt(I)</u> <u>$[CoH(C_2H_4\{PPh_2\}_2)_2]$</u> was prepared from dibromodi-{1,2-bis(diphenylphosphino)ethane}cobalt and sodium borohydride both in absolute ethanol, as the corresponding rhodium-derivative, and, according Chatt[5], in 3:1 ethanol-water

solution. Diamagnetic red plates, m.p. 237-40°, decomp. 280°. (Found: C, 72.8; H, 5.86; P, 14.5; $C_{62}H_{49}CoP_4$ requires C, 72.90; H, 5.77; P, 14.46%).

<u>Reactions of the Hydrido-complexes. (1) Reaction with perchloric acid</u>. The hydrido-complex of rhodium (0.1374 g.) was trated in an evacuated apparatus with a solution (5 c.c.) of 1 M perchloric acid in ethanol(80%)-water, and the evolved gas (4.00 c.c. at 20° and 750 mm) collected. Molar ratio, hydrogen to complex, equal to 1.06. The solid residue, filtered off, washed with ethanol and dried, was identified as di-{1,2-bis(diphenylphosphino)ethane}rhodium(I) perchlorate by its infrared spectrum, m.p. and analysis. (Found: Cl, 3.72%).
<u>(2) Reaction with hydrogen chloride.</u> The hydrido-complex of rhodium (0.1312 g.), treated, as described above, with a 1 M solution (5 c.c.) of hydrogen chloride in ethanol(80%)-water, gave off hydrogen (3.60 c.c at 20° and 750 mm) in a molar ratio hydrogen to complex of 0.997. Another sample of the hydrido-complex (2.0 g.), suspended in ethanol (15 c.c.), was treated with the 1 M solution (10 c.c.) of hydrogen chloride in aqueous ethanol under nitrogen. After the effervescence ceased, the solvent was removed under vacuum and the residue recrystallized from benzene, yielding a light yellow crystalline compound, m.p. 180-2°, soluble in organic polar solvents, rather soluble in benzene, diamagnetic. (Found: C, 61.15; H, 5.26; Cl, 7.14; $C_{52}H_{49}Cl_2P_4Rh$ requires

C, 6?.?7; H, 5.08; Cl, 7.??%). Molar conductivity 10^{-3} M in nitro=benzene at 25°: λ_m = 17.8 mhos.

(?) Reaction with carbon tetrachloride. The hydrido-complexes of rhodium and of cobalt (0.1 g.) were treated with carbon tetrachloride (0.25 c.c.) under nitrogen. After a few minutes, the solvent was distilled under vacuum, collecting it in a dry-ice trap, and its infrared spectrum recorded using 0.I mm cells and pure carbon tetrachloride as reference. The presence of the chloroform in the solvent was proved by the bands at 1217 and 668 cm^{-1}.

Reaction of di-{1,2-bis(diphenylphosphino)ethane}rhodium(I) chloride with hydrogen chloride. A solution of $[Rh(DPE)_2]Cl$ (?.0 .) in ethanol (?0 c.c.) was treated as under (?) with a 1 ? solution of hydrogen chloride in aqueous ethanol (10 c.c.). After removal of the solvent under vacuum and recrystallisation of the residue from benzene, the light yellow product was identified by its infrared spectrum, m.p., conducti=vity in nitrobenzene (λ_m = 17.6 mhos), diamagnetism and analysis (found: C, 6?.3; H, 5.18; Cl, 6.97%) as the same compound as obtained under (?). By treatment with sodium tetraphenylborate in ethanolic solution, it gave a light yellow precipitate, m.p. 234°, slightly soluble in ethanol. (Found: C, 71.5; H, 5.65; Cl, 2.75; $C_{76}H_{69}BClP_4Rh$ requires C, 72.64;

H, 5.61; Cl, 2.82%).

Determination of Dipole Moments. These were determined as described previously[11] and are listed in the Table.

	w_2	$\Delta\varepsilon$	Δv	α_0	β	P_T	P_E	μ(D)	μ_{20}(D)
$RhH(DPE)_2$	0.01192	0.03305	-0.0049	2.77	-0.41	666.5	274	4.35	4.03
	0.01360	0.03688	-0.0056	2.71	-0.41	656.0	274		
$CoH(DPE)_2$	0.00832	0.01877	-0.0037	2.25	-0.45	539.3	274		
	0.00952	0.01954	- 0.0044	2.05	-0.46	506.8	274	3.50	3.08

Aknowledgment. The authors gratefully thank Dr. Anna Segrè for the nuclear magnetic resonance spectra.

This research was supported in whole by the U.S. Air Force under Grant N° AF-EOAR 6234 and monitored by European Office, Office of Airspace Research.

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